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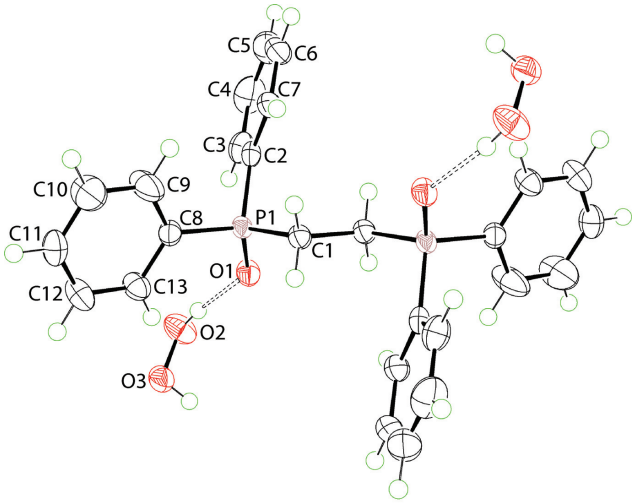
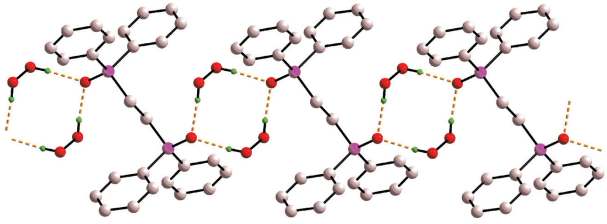
Crystal structure of ethane-1,2-diylbis (diphenylphosphine oxide) – dihydrogenperoxide (1/2), $C_{26}H_{28}O_6P_2$





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Abstract

$C_{26}H_{28}O_6P_2$, monoclinic, $C2/c$ (no. 15), $a = 12.8582(1)$ Å, $b = 12.4664(1)$ Å, $c = 15.4358(1)$ Å, $\beta = 95.738(1)°$, $V = 2461.89(3)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0296$, $wR_{ref}(F^2) = 0.0809$, $T = 100(2)$ K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.21 × 0.18 × 0.16 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	1.94 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	15092, 2209, 0.023
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2150
$N(param)_{refined}$:	160
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
P1	0.63489(2)	0.26828(3)	0.59742(2)	0.01656(13)
O1	0.59865(7)	0.38168(7)	0.58138(6)	0.0237(2)
O2	0.43878(8)	0.50768(9)	0.61936(7)	0.0340(3)
H2O	0.4859(13)	0.4626(14)	0.6090(13)	0.051*
O3	0.35955(8)	0.48151(8)	0.54863(7)	0.0288(2)
H3O	0.3763(15)	0.5234(14)	0.5092(10)	0.043*
C1	0.70133(10)	0.21716(10)	0.50803(8)	0.0189(3)
H1A	0.722360	0.141903	0.520530	0.023*
H1B	0.652174	0.217443	0.454403	0.023*
C2	0.72539(10)	0.25872(11)	0.69350(9)	0.0191(3)
C3	0.72370(12)	0.33851(12)	0.75690(9)	0.0271(3)
H3	0.673794	0.394817	0.749830	0.033*
C4	0.79545(14)	0.33498(15)	0.83033(10)	0.0392(4)
H4	0.794386	0.388761	0.873841	0.047*
C5	0.86859(13)	0.25311(16)	0.84022(10)	0.0404(4)
H5	0.918517	0.252028	0.889932	0.048*
C6	0.86953(11)	0.17316(15)	0.77849(10)	0.0330(4)
H6	0.919017	0.116537	0.786364	0.040*
C7	0.79819(10)	0.17552(12)	0.70497(9)	0.0242(3)
H7	0.798836	0.120552	0.662406	0.029*
C8	0.52740(10)	0.17782(11)	0.60555(8)	0.0199(3)
C9	0.54213(13)	0.07445(14)	0.63811(14)	0.0473(5)
H9	0.610143	0.051141	0.659748	0.057*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C10	0.45788(14)	0.00518(14)	0.63914(15)	0.0505(5)
H10	0.468471	−0.065331	0.661640	0.061*
C11	0.35935(11)	0.03781(12)	0.60787(10)	0.0289(3)
H11	0.301837	−0.009874	0.608741	0.035*
C12	0.34422(11)	0.13987(12)	0.57526(10)	0.0294(3)
H12	0.276095	0.162318	0.553135	0.035*
C13	0.42762(11)	0.21037(12)	0.57440(10)	0.0247(3)
H13	0.416277	0.281034	0.552429	0.030*

Source of material

1,2-Bis(diphenylphosphino)ethane (Sigma-Aldrich, 0.98 g, 2.5 mmol) was dissolved in 95% ethanol (100 mL). To this solution was added 30% hydrogen peroxide in excess (Merck, 0.50 mL). The mixture was stirred at room temperature for 1 h and filtered. The filtrate was evaporated slowly at room temperature until white crystalline solids were formed. Yield: 0.84 g (68.7%). **M. pt** (Stuart SMP30 digital melting point apparatus; uncorrected): 420–422 K. **IR** (Bruker Vertex 70v FTIR Spectrometer; cm^{-1}): 3206 (b) ν(O–H), 1465 (s) ν(C=C), 1185 (m) ν(P=O), 1088 (m) ν(P–Ar). **^{1}H NMR** (Bruker Ascend 400 MHz NMR spectrometer; $CDCl_3$; ppm relative to Me_4Si): δ 1.86 (s, 2H, OH), 2.51 (s, 4H, CH_2), 7.43–7.72 (20H, Ph—H). **^{13}C{^{1}H} NMR** (as for ^{1}H NMR): 21.9 (d, CH_2, J = 66 Hz) 128.8, 130.8, 131.2, 131.9, 132.4, 132.6 (Ph—C).

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95–0.99 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(C). The O-bound H atoms were refined with O—H = 0.84 ± 0.01 Å, and with U_{iso}(H) = 1.5U_{eq}(O).

Comment

The title compound $Ph_2P(=O)CH_2CH_2P(=O)Ph_2 \cdot 2H_2O_2$, (I), was generated during a successful attempt to oxidise $Ph_2PCH_2CH_2PPh_2$ for the purpose of coordinating the oxidised species to various neutral organotin species, studies which, hitherto, have focussed upon mono-functional triorganophosphaneoxide adducts [5, 6].

The molecular structures of the constituents of (I) are shown in the upper part of the figure (70% displacement ellipsoids; unlabelled atoms are related by the symmetry operation (i) 3/2 − *x*, 1/2 − *y*, 1 − *z*). The ethane-1,2-diylbis (diphenylphosphine oxide) molecule is disposed about a centre of inversion located at the mid-point of the C1—C1^i bond. The P1 atom is tetrahedrally coordinated by methylene-C [P1—C1 = 1.8099(13) Å], phenyl-C [P1—C2, C8 = 1.7951(14) & 1.7978(13) Å] and oxide-O1 [P1—O1 = 1.5013(9) Å] atoms. The angles in the C_3O donor set range from a narrow 104.90(6)°, for C1—P1—C8, to a wide 111.97(6)° for C8—P1—O1; the angles involving the O1 atom are uniformly wider than those involving C atoms only. The O2—O3 bond in the hydrogen peroxide molecule is 1.4539(15) Å.

While there are several triorganophosphaneoxide analogues of (I) in the crystallographic literature, the most closely related structure is that of the only diphosphane analogue, i.e. $Cy_2P(=O)CH_2CH_2P(=O)Cy_2 \cdot H_2O_2$ [7]. Here, the diphosphane molecule is disposed about a centre of inversion, as for (I), but crystallises with only one H_2O_2 molecule per diphosphane species.

In the crystal and as shown in the lower view of the figure, the hydrogen peroxide molecule employs both hydrogen atoms to bridge oxide atoms of translationally-related molecules [O2—H2o···O1: H2o···O1 = 1.851(17) Å, O2···O1 = 2.6977(14) Å with angle at H2o = 171.7(18)° and O3—H3o···O1^{ii}: H3o···O1^{ii} = 1.884(16) Å, O3···O1^{ii} = 2.7278(14) Å with angle at H3o = 175.1(19)° for (ii) 1 − *x*, 1 − *y*, 1 − *z*]. The hydrogen bonding results in a linear, supramolecular chain sustained by 10-membered {···HOOH···O}$_2$ synthons which have a chair conformation; the chain is close to being parallel to [1 −1 0]. As the chains appear to pack in the crystal without directional interactions between them, the molecular packing was further analysed by calculating the Hirshfeld surfaces as well as the full- and delineated two-dimensional fingerprint plots for the individual molecules using the program Crystal Explorer 17 [8] and standard protocols [9]. There are only two types of contributors to the calculated Hirshfeld surface of the H_2O_2 molecule, namely H···O/O···H which makes up 66.7% of all contacts with the remainder, i.e. 33.3%, being due to H···H contacts. For the diphosphane molecule, the contribution from H···H contacts increases to 54.8% with H···O/O···H contacts accounting for 17.0% of all contacts. The only other contributions to the surface are from H···C/C···H [20.4%] and C···C [7.8%] contacts.

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